IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

OKINAKA ET AL.

SERIAL NO. 09/878,311 GROUP ART UNIT: 1742

FILED: June 12, 2001 EXAMINER: J. P. SHEEHAN

FOR: SPINDLE-SHAPED GOETHITE PARTICLES, SPINDLE-SHAPED HEMATITE PARTICLES, SPINDLE-SHAPED MAGNETIC METAL PARTICLES CONTAINING IRON AS MAIN COMPONENT AND PROCESSES FOR PRODUCING THE SAME

DECLARATION UNDER 37 C.F.R. 1.132

HONORABLE COMMISSIONER OF PATENTS & TRADEMARKS

WASHINGTON, D.C. 20231

SIR:

Now comes Kenji OKINAKA, a citizen of Japan, and a resident of 56-4, Tsumasaki-Kaisaku, Ube-shi, Yamaguchi-ken, Japan, who declares and says that:

1. I graduated from the Department of Technochemistry, Faculty of Technology, Ehime University in March, 1986.

2. I am currently employed by TODA KOGYO CORPORATION since April, 1986.

3. I am familiar with the work related to U.S. Patent Application, Serial No. 09/878,311, and am a co-inventor of U.S. Patents: No. 5,156,922, No. 5,238,483, No. 5,466,306,

No. 5,531,922, No. 5,599,378, No. 5,645,652 and No. 5,735,969, No. 6,391,450 and No.6,720,094.

4. I have read the Office Action dated March 9, 2004, have understand the Examiner's rejection to the invention claimed in the above application, and have ascertained the following.

5. I have calculated an atomic ratio of Al to Co of spindle-shaped iron-based alloy particles of the following Reference Examples 1 to 6 of OKINAKA (EP 0 940 369).

<Production of spindle-shaped goethite particles>

Example 1 of OKINAKA:

30 liters of a mixed aqueous alkali solution containing sodium carbonate in amounts of 25 mol and sodium hydroxide in amounts of 18 mol (the concentration of sodium hydroxide being equivalent to 26.5 mol % (calculated as normality) based on mixed alkali) were charged into a bubble tower and the temperature thereof was adjusted to 47°C while passing a nitrogen gas through the bubble tower at a linear velocity of 2.21 cm/s. Then, 20 liters of an aqueous ferrous sulfate solution containing 20 mol of $Fe^{2+}$ (the concentration of the mixed aqueous alkali solution being equal to 1.7 equivalents (calculated as normality) based on the ferrous sulfate) to which an aqueous aluminum sulfate solution containing 2.0 mol of $Al^{3+}$ (equivalent to 10 atm % (calculated as Al) based on whole Fe) had been preliminarily added, were charged into the bubble tower and the contents of the bubble tower were

aged therein for 300 minutes. Thereafter, 2 liters of an aqueous cobalt sulfate solution containing 2.0 mol of $Co^{2+}$ (equivalent to 10 atm % (calculated as Co) based on whole Fe) was added to the bubble tower. After air was passed through the bubble tower at a linear velocity of 1.99 cm/sec to conduct the oxidation reaction, the resultant reaction mixture was washed with water using a filter press until the electric conductivity reached 60 µS, thereby obtaining a press cake.

A part of the obtained press cake was dried and pulverized by an ordinary method, thereby obtaining goethite particles. As recognized from the transmission electron micrograph, the obtained goethite particles were of a spindle shape, and had a BET specific surface area of 110.5 $m^2/g$, an average major axial diameter of 0.128 µm, a standard deviation $\sigma$ of 0.0248 µm, a particle size distribution (standard deviation/average major axial diameter) of 0.194, an average minor axial diameter of 0.0149 µm and an aspect ratio (average major axial diameter/average minor axial diameter) of 8.6:1. Further, the obtained goethite particles contained no dendritic particles, and had $D_{020}$ of 17.6 nm, $D_{110}$ of 11.4 nm and a ratio of $D_{020}/D_{110}$ of 1.54:1. The obtained goethite particles were composed of 48.2 % by weight of Fe, 5.08 % by weight of cobalt and 2.32 % by weight of aluminum. Further, it was determined that the cobalt content was 10 atm % (calculated as Co) based on whole Fe, and the aluminum

content was 10 atm % (calculated as Al) based on whole Fe.

Examples 2 & 3 and Comparative Example 8 of OKINAKA:

The same procedure as defined in Example 1 was conducted except that production conditions of the spindle-shaped goethite particles were varied as shown in Table 1, thereby obtaining spindle-shaped goethite particles. Various properties of the obtained spindle-shaped goethite particles are shown in Table 2.

Comparative Example 4 of OKINAKA:

The same procedure as defined in Example 1 was conducted except that the cobalt compound to be added upon the production reaction of goethite particles was added to the aqueous ferrous salt solution, and the aluminum compound was added immediately after the passage of the aging period, thereby producing goethite particles.

It was determined that the obtained goethite particles were ultrafine particles.

Comparative Example 5 of OKINAKA:

The same procedure as defined in Example 1 was conducted except that both the cobalt compound to be added upon the production reaction of goethite particles and the aluminum compound were added immediately after the passage of the aging period, thereby producing goethite particles.

It was determined that the obtained goethite particles

were ultrafine particles.

<Production of spindle-shaped magnetic iron-based alloy particles>

Reference Example 1 of OKINAKA:

The press cake containing 1,000 g (8.68 mol as Fe) of the spindle-shaped goethite particles obtained in Example 1 was sufficiently dispersed in 40 liters of water. 2 liters of an aqueous yttrium nitrate solution containing 266 g of yttrium nitrate hexahydrate (equivalent to 8 atm % (calculated as Y) based on whole Fe in the goethite particles) and 4 liters of an aqueous cobalt acetate solution containing 435 g of cobalt acetate tetrahydrate were added to the obtained dispersion, and then stirred. Further, after a 25.0 wt% aqueous sodium carbonate solution as a precipitating agent was added to adjust the pH of the dispersion to 9.5, the resultant dispersion was washed with water using a filter press. The obtained press cake was extrusion-molded using a compression molding machine equipped with a mold plate having an orifice diameter of 3 mm, followed by drying at 120°C, thereby obtaining goethite particles coated with the yttrium compound and the cobalt compound. The cobalt content in the obtained goethite particles was 25 atm % (calculated as Co) based on whole Fe; the aluminum content thereof was 10 atm % (calculated as Al) based on whole Fe; and the yttrium content thereof was 8 atm % (calculated as Y) based on whole Fe. Further, it was

determined that yttrium existed only in an outer layer portion of each particle.

The spindle-shaped goethite particles coated with the yttrium compound and the cobalt compound were heat-dehydrated in air at 600° C, thereby producing spindle-shaped hematite particles having an outer layer composed of the yttrium compound and the cobalt compound.

100 g of the thus obtained spindle-shaped hematite particles having the outer layer composed of the yttrium compound and the cobalt compound were charged into a fixed bed reducing apparatus having an inner diameter of 72 mm. While a hydrogen ($H_2$) gas was passed through the reducing apparatus at a flow rate of 35 liter/min, the spindle-shaped hematite particles were heat-reduced at 600° C. After the hydrogen gas was replaced with a nitrogen gas, the particles were cooled to 80° C, and then the oxygen partial pressure in the reducing apparatus was gradually increased by passing a water vapor therethrough until the oxygen content therein reached the same content as in air, thereby forming a stable oxide film on the surface of each particle.

As recognized from the transmission electron micrograph, the obtained spindle-shaped magnetic iron-based alloy particles and further containing cobalt, aluminum and yttrium, had an average major axial diameter of 0.102 μm, a standard deviation σ of 0.0157 μm, a particle size distribution (standard deviation/average major axial diameter) of 0.154, an average minor axial diameter of

0.0128 µm, an aspect ratio (average major axial diameter:average minor axial diameter) of 8.0:1, a BET specific surface area of 48.2 $m^2/g$ and an X-ray crystallite size $D_{110}$ of 15.7 nm. In addition, the spindle-shaped magnetic iron-based alloy particles had a spindle shape and a uniform particle size, and contained much less amount of dendritic particles. Further, the cobalt content in the particles was 25 atm % (calculated as Co) based on whole Fe; the aluminum content was 10 atm % (calculated as Al) based on whole Fe; and the yttrium content was 8 atm % (calculated as Y) based on whole Fe. As to the magnetic properties of the obtained magnetic iron-based alloy particles, the coercive force thereof was as high as 2,274 Oe; the saturation magnetization $\sigma s$ was 141.3 emu/g; the squareness ($\sigma r/\sigma s$) was 0.541; and the oxidation stability $\Delta\sigma s$ of the saturation magnetization was 3.2 % (as an absolute value) (measured value: -3.2 %). Further, as to sheet magnetic characteristics, the sheet coercive force Hc was 2,326 Oe; the sheet squareness (Br/Bm) was 0.868; the sheet SFD was 0.354; and $\Delta$Bm was 2.0 %.

Reference Examples 2 to 6 of OKINAKA:

The same procedure as defined in Reference Example 1 was conducted except that kind of particles to be treated, kind and amount of the coating material used for the anti-sintering treatment, the heating temperature and the reducing temperature upon the heat-reduction step were

varied, thereby producing magnetic iron-based alloy particles. Heat-dehydration conditions and heat-reduction conditions are shown in Table 3, and various properties of the obtained magnetic iron-based alloy particles are shown in Table 4.

Table 1

| Examples and Comparative Examples | Production of spindle-shaped goethite particles | | | | |
|---|---|---|---|---|---|
| | Mixed aqueous alkali solution | | | | |
| | Aqueous alkali carbonate solution | | Aqueous alkali hydroxide solution | | Alkali ratio: 1/2· alkali hydroxide /whole alkali (%) |
| | Kind | Amount used (mol) | Kind | Amount used (mol) | |
| Example 2 | $Na_2CO_3$ | 25 | NaOH | 18 | 26.5 |
| Example 3 | $Na_2CO_3$ | 25 | NaOH | 18 | 26.5 |
| Comp. Ex. 4 | $Na_2CO_3$ | 25 | NaOH | 18 | 26.5 |
| Comp. Ex. 5 | $Na_2CO_3$ | 25 | NaOH | 18 | 26.5 |
| Comp. Ex. 8 | $Na_2CO_3$ | 25 | NaOH | 18 | 26.5 |

Table 1 (continued)

| Examples and Comparative Examples | Production of spindle-shaped goethite particles | | | | | |
|---|---|---|---|---|---|---|
| | Aqueous ferrous salt solution | | Equivalent ratio: whole alkali/ $Fe^{2+}$ note 1) | Aging | | |
| | Kind | Amount used (mol) | | Temperature (°C) | Time (hr) | Linear velocity of nitrogen passed (cm/s) |
| Example 2 | $FeSO_4$ | 20 | 1.70 | 47 | 5 | 2.21 |
| Example 3 | $FeSO_4$ | 20 | 1.70 | 47 | 5 | 2.21 |
| Comp. Ex. 4 | $FeSO_4$ | 20 | 1.70 | 47 | 5 | 2.21 |
| Comp. Ex. 5 | $FeSO_4$ | 20 | 1.70 | 47 | 5 | 2.21 |
| Comp. Ex. 8 | $FeSO_4$ | 20 | 1.70 | 47 | 5 | 2.21 |

Note 1: calculated assuming that the whole alkali was composed of (1/2 x alkali hydroxide + alkali carbonate).

Table 1 (continued)

| Examples and Comparative Examples | Production of spindle-shaped goethite particles | | |
|---|---|---|---|
| | Aluminum compound | | |
| | Kind | Amount added (mol) | Timing of addition |
| Example 2 | Aluminum sulfate | 1.0 | Aqueous ferrous salt solution |
| Example 3 | Aluminum sulfate | 0.6 | Aqueous ferrous salt solution |
| Comp. Ex. 4 | Aluminum sulfate | 2.0 | After the passage of aging period |
| Comp. Ex. 5 | Aluminum sulfate | 2.0 | After the passage of aging period |
| Comp. Ex. 8 | Aluminum sulfate | 2.0 | Aqueous ferrous salt solution |

Table 1 (continued)

| Examples and Comparative Examples | Production of spindle-shaped goethite particles | | |
|---|---|---|---|
| | Cobalt compound | | |
| | Kind | Amount added (mol) | Timing of addition |
| Example 2 | Cobalt sulfate | 3.0 | After the passage of aging period |
| Example 3 | Cobalt sulfate | 0.6 | After the passage of aging period |
| Comp. Ex. 4 | Cobalt sulfate | 2.0 | Aqueous ferrous salt solution |
| Comp. Ex. 5 | Cobalt sulfate | 2.0 | After the passage of aging period |
| Comp. Ex. 8 | Cobalt sulfate | 2.0 | Aqueous ferrous salt solution |

Table 1 (continued)

| Examples and Comparative Examples | Production of spindle-shaped goethite particles | |
|---|---|---|
| | Linear velocity of air passed (cm/s) | Temperature (°C) |
| Example 2 | 1.99 | 47 |
| Example 3 | 1.99 | 47 |
| Comp. Ex. 4 | 1.99 | 47 |
| Comp. Ex. 5 | 1.99 | 47 |
| Comp. Ex. 8 | 1.99 | 47 |

Table 2

| Examples and Comparative Examples | Properties of goethite particles | |
|---|---|---|
| | Kind | Shape |
| Example 2 | Goethite particles | Spindle-shaped |
| Example 3 | Goethite particles | Spindle-shaped |
| Comp. Ex. 4 | Goethite particles | Spindle-shaped |
| Comp. Ex. 5 | Goethite particles | Spindle-shaped |
| Comp. Ex. 8 | Goethite particles | Spindle-shaped |

Table 2 (continued)

| Examples and Comparative Examples | Properties of goethite particles | | |
|---|---|---|---|
| | Average major axial diameter: l (μm) | Standard deviation: σ | particle size distribution: σ/l |
| Example 2 | 0.120 | 0.0235 | 0.196 |
| Example 3 | 0.145 | 0.0264 | 0.182 |
| Comp. Ex. 4 | 0.102 | 0.0226 | 0.222 |
| Comp. Ex. 5 | 0.042 | 0.0098 | 0.233 |
| Comp. Ex. 8 | 0.212 | 0.0563 | 0.266 |

Table 2 (continued)

| Examples and Comparative Examples | Properties of goethite particles | | |
|---|---|---|---|
| | Average minor axial diameter (μm) | Aspect ratio | BET specific surface area ($m^2/g$) |
| Example 2 | 0.0141 | 8.5:1 | 131.0 |
| Example 3 | 0.0173 | 8.4:1 | 85.9 |
| Comp. Ex. 4 | 0.0212 | 4.8:1 | 215.7 |
| Comp. Ex. 5 | 0.0072 | 5.8:1 | 267.3 |
| Comp. Ex. 8 | 0.0462 | 4.6:1 | 65.6 |

Table 2 (continued)

| Examples and Comparative Examples | Properties of goethite particles | | | | |
|---|---|---|---|---|---|
| | Co content: Co/Fe (atm %) | Al content: Al/Fe (atm %) | X-ray crystallite size | | |
| | | | $D_{020}$ (nm) | $D_{110}$ (nm) | $D_{020}/D_{110}$ |
| Example 2 | 15.0 | 5.0 | 17.1 | 10.3 | 1.66 |
| Example 3 | 3.0 | 3.0 | 18.8 | 12.6 | 1.49 |
| Comp. Ex. 4 | 10.0 | 10.0 | 8.3 | 7.2 | 1.15 |
| Comp. Ex. 5 | 10.0 | 10.0 | 7.2 | 6.2 | 1.16 |
| Comp. Ex. 8 | 10.0 | 10.0 | 23.4 | 10.9 | 2.15 |

Table 3

| Reference Examples | Kind of starting goethite particles | Production conditions of magnetic iron-based alloy particles | | | |
|---|---|---|---|---|---|
| | | Anti-sintering agent | | | |
| | | Rare earth compound | | Other compound | |
| | | Kind | Amount added R/Fe (mol%) | Kind | Amount added M/Fe (mol%) |
| Reference Example 2 | Example 2 | Neodymium nitrate | 5.0 | Cobalt sulfate | 5.0 |
| Reference Example 3 | Example 3 | Neodymium nitrate | 3.0 | Cobalt sulfate<br>Aluminum sulfate | 7.0<br>7.0 |
| Reference Example 4 | Com. Ex.4 | Yttrium nitrate | 8.0 | Cobalt sulfate | 15.0 |
| Reference Example 5 | Com. Ex.5 | Yttrium nitrate | 8.0 | Cobalt sulfate | 15.0 |
| Reference Example 6 | Com. Ex.8 | Yttrium nitrate | 8.0 | Cobalt sulfate | 15.0 |

Table 3 (continued)

| Reference Examples | Production conditions of magnetic iron-based alloy particles | | |
|---|---|---|---|
| | Heat-treatment | | Heat-reduction |
| | Heating temperature (°C) | Atmosphere | Temperature (°C) |
| Reference Example 2 | 650 | Air | 500 |
| Reference Example 3 | 700 | Air | 600 |
| Reference Example 4 | 600 | Air | 600 |
| Reference Example 5 | 600 | Air | 600 |
| Reference Example 6 | 600 | Air | 600 |

Table 4

| Reference Examples | Properties of magnetic iron-based alloy particles | | | |
|---|---|---|---|---|
| | Shape | Average major axial diameter : l (μm) | Standard deviation : σ | particle size distribution: σ/l |
| Reference Example 2 | Spindle-shaped | 0.098 | 0.0147 | 0.150 |
| Reference Example 3 | Spindle-shaped | 0.121 | 0.0196 | 0.162 |
| Reference Example 4 | Spindle-shaped | 0.075 | 0.0167 | 0.223 |
| Reference Example 5 | Spindle-shaped | 0.038 | 0.0123 | 0.324 |
| Reference Example 6 | Spindle-shaped | 0.198 | 0.0463 | 0.234 |

Table 4 (continued)

| Reference Examples | Properties of magnetic iron-based alloy particles | | | |
|---|---|---|---|---|
| | Average minor axial diameter (μm) | Aspect ratio | BET specific surface area ($m^2/g$) | X-ray crystallite size ($D_{110}$) (nm) |
| Reference Example 2 | 0.0124 | 7.9:1 | 49.1 | 16.2 |
| Reference Example 3 | 0.0155 | 7.8:1 | 40.6 | 15.9 |
| Reference Example 4 | 0.0188 | 4.0:1 | 63.8 | 16.2 |
| Reference Example 5 | 0.0087 | 4.4:1 | 74.5 | 13.2 |
| Reference Example 6 | 0.0492 | 4.0:1 | 65.5 | 18.4 |

Table 4 (continued)

| Reference Examples | Properties of magnetic iron-based alloy particles | | |
|---|---|---|---|
| | Co content: Co/Fe (atm %) | Al content: Al/Fe (atm %) | Content of rare earth element: Re/Fe (atm %) |
| Reference Example 2 | 20 | 5 | 5 |
| Reference Example 3 | 10 | 10 | 3 |
| Reference Example 4 | 25 | 10 | 8 |
| Reference Example 5 | 25 | 10 | 8 |
| Reference Example 6 | 25 | 10 | 8 |

Table 4 (continued)

| Reference Examples | Properties of magnetic iron-based alloy particles | | | |
|---|---|---|---|---|
| | Coercive force Hc (Oe) | Saturation magnetization : $\sigma s$ (emu/g) | Squareness : $\sigma r/\sigma s$ | $\Delta\sigma s$ (%) |
| Reference Example 2 | 2,180 | 145.6 | 0.540 | 4.5 |
| Reference Example 3 | 1,921 | 140.6 | 0.535 | 4.6 |
| Reference Example 4 | 1,527 | 112.4 | 0.486 | 12.6 |
| Reference Example 5 | 1,621 | 102.1 | 0.489 | 16.3 |
| Reference Example 6 | 1,426 | 118.2 | 0.483 | 13.8 |

Remarks

As seen from the above data, the atomic ratios of Al to Co of spindle-shaped iron-based alloy particles of Reference Examples 1 to 6 of OKINAKA are set forth below.

| | Atomic ratio of Al to Co (-) |
|---|---|
| Reference Example 1 | 10/25=0.4 |
| Reference Example 2 | 5/20=0.25 |
| Reference Example 3 | 10/10=1.0 |
| Reference Example 4 | 10/25=0.4 |
| Reference Example 5 | 10/25=0.4 |
| Reference Example 6 | 10/25=0.4 |

As seen from the above, spindle-shaped iron-based alloy particles of the Reference Examples 1 to 6 have the atomic ratios of Al to Co of 0.4 to 1.0, which are out of the range of our invention. Further, the coercive forces of such spindle-shaped iron-based alloy particles of the Reference Examples 1 to 3 is 1921 to 2274 Oe, which are out of the range of our invention. In addition, the spindle-shaped iron-based alloy particles of the Reference Examples 4 to 6 have an aspect ratios of 4.0:1 to 4.4:1 and an oxidation stability of saturation magnetization ($\Delta\sigma s$) of 12.6 to 16.3, which are out of the range of our invention.

Therefore, the combination of (1) the atomic ratio of Al to Co of from more than 2 to 4 and the coercive force of 111.4 to 143.2 kA/m (1,400 to 1,800 Oe) of the present invention can not been forecasted from the Reference Examples 1 to 3 of OKINAKA.

In addition, the combination of (1) the atomic ratio of Al to Co of from more than 2 to 4 and the oxidation stability of saturation magnetization ($\Delta\sigma s$) of not more than 10% of the present invention can not been forecasted from the Reference Examples 4 to 6 of OKINAKA.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: July 12, 2004

Kenji Okinaka

Kenji OKINAKA